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Bimetallic Cu-Ni nanoparticles supported on activated carbon for catalytic oxidation of benzyl alcohol

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ABSTRACT

A series of bimetallic copper-nickel ($CuNi_x$, x = 0.1, 0.2, 0.5 and 1) nanoparticles supported on activated carbon (AC) were prepared by deposition-precipitation method for the oxidation of benzyl alcohol to benzaldehyde using hydrogen peroxide as oxidising agent. Analyses by means of X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) confirmed that Cu and Ni was successfully added on the surface of activated carbon. $CuNi_1$/AC showed the best catalytic activity for the oxidation of benzyl alcohols to the corresponding aldehyde within a short reaction period at 80 °C. The catalytic performance is significantly enhanced by the addition of equal amount of Ni as compared to the monometallic counterpart. This result indicates the synergistic effect between Ni and Cu particles in the catalytic oxidation reaction.

1. Introduction

The oxidation of benzyl alcohol to benzaldehyde is one of the most essential functional group transformations. Benzaldehyde is commonly used as a starting material in the preparation of perfumery and pharmaceutical [1,2]. The usage of conventional routes to produce benzaldehyde involves the release of pollutants, thus direct oxidation of liquid benzyl alcohol is widely investigated [3–5]. Therefore, the development of effective and efficient catalysts for this approach utilizing mild reaction conditions at low reaction temperature is been done [3–5].

Noble metals such as Au [6,7] and Pd [8] have shown their potentials to fulfil this requirement. However, these catalysts are expensive thus hinders wide application. Recently, focus has been made on the usage of transition metals as catalyst [9–15]. It has been reported that Cu [9] and Ni [10,11] catalyst both has high conversion towards the oxidation of benzyl alcohol to benzaldehyde. Ni is usually added as the second metal for the oxidation of benzyl alcohol as reported for Mn/Ni [12] and Ni/Mg [13]. The role of Ni was found to provide sites for oxygen activation [12]. Bimetallic Cu-Mn [14], Cu-Au [15] have showed superior catalytic performance in the oxidation of benzyl alcohol to benzaldehyde compared to those of their monometallic counterparts because of their tunable and synergistic effect. Therefore, we aim to investigate the role of Ni incorporated into Cu lattice which might change the physicochemical properties of bimetallic catalyst.

Catalytic properties are also strongly dependent on their composition, size and interaction with support. Herein, activated carbon was used as the catalyst support due to its advantageous features such as large surface area [16] and good chemical stability [17]. Activated carbon also plays a role in maintaining the catalytic active phase in a highly dispersed state [18]. In this study, a series of bimetallic $CuNi_x$ (x = 0.1, 0.2, 0.5 and 1) nanoparticles supported on activated carbon was prepared using deposition-precipitation method to evaluate the effect of different ratios of Ni added into Cu catalyst. The comparison between monometallic Cu and Ni nanoparticles and bimetallic Cu-Ni nanoparticles were also done. The catalytic activity of these catalysts was evaluated for the oxidation of benzyl alcohol to benzaldehyde using hydrogen peroxide as an oxidant. The results show that the addition of Ni at optimum amount to Cu catalyst demonstrates the dual role of Cu and Ni towards the catalytic activity of aerobic benzyl alcohol oxidation reaction.

2. Experimental

2.1. Preparation of catalysts

The $CuNi_x$/AC (x = 0.1, 0.2, 0.5, 1) nanoparticles catalyst were prepared by using homogeneous deposition-precipitation method previously reported with slight modification [19]. In brief, for the synthesis of $CuNi_{0.1}$/AC catalyst, 1.0 g of AC was added into 50 mL aqueous solution

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of 0.1 mol of $Cu(NO_3)_2{\cdot}3H_2O$ and 0.01 mol of $Ni(NO_3)_2{\cdot}6H_2O$ under stirring at room temperature. The resulting mixture was stirred for 15 min and 0.1 mol L^{-1} of NaOH was added dropwise, under vigorous stirring at room temperature until the pH becomes 10.0. The resulting solution was aged at room temperature for 24 h, centrifuged and washed with deionized water until neutral pH. The prepared sample was dried at 110 °C overnight followed by calcination at 500 °C in air for 3 h. To compare the catalytic activity, single metal catalyst Cu/AC and Ni/AC catalysts was also prepared using the same method.

2.2. Characterisation of catalysts

X-ray Diffraction (XRD) patterns of the catalysts were obtained by D8 Advance (BRUKER AXS, Germany) diffractometer using Cu Kα radiation (λ = 1.541 Å) from 10° to 80° to investigate the structural properties. Scanning Electron Microscope (SEM) images were taken using JSM-6390 (JEOL, USA) to identify the morphology and estimate the particle size of the catalysts.

2.3. Evaluation of catalytic performance

Liquid phase oxidation of benzyl alcohol was carried out using procedures that was reported previously with slight modification [20]. In a typical reaction, 2.6 mL (25 mmol) of benzyl alcohol, 3.3 mL (32 mmol) of 30% H_2O_2 and 0.1 g of the catalyst powder was loaded in a 50 mL double neck round bottom flask containing 20 mL of toluene as solvent. The flask was connected to a reflux condenser, magnetically stirred and kept in an oil bath at 80 °C for 2 h. After reaction, the solid catalysts were separated by centrifugation and the liquid samples were filtered and analysed by gas chromatography to evaluate the products by GC-MS (SHIDMADZU QP 5000) equipped with a flame ionization detector (FID) and a medium polarity capillary column (BPX-5 column (29.4 m × 0.25 mm), with film thickness of 0.25 μm) with helium as the carrier gas.

3. Results and discussion

3.1. Crystal structure of catalysts

The XRD patterns of Cu/AC, Ni/AC and $CuNi_x$/AC (x = 0.1, 0.2, 0.5, 1) nanoparticles are shown in Fig. 1. The weak diffraction peak at 2θ = 26.5° was assigned to the activated carbon support [21] with hexagonal phase according to PDF no. 01-071-3739. The structure for AC remains the same even after modifications with Cu, Ni and $CuNi_x$. The

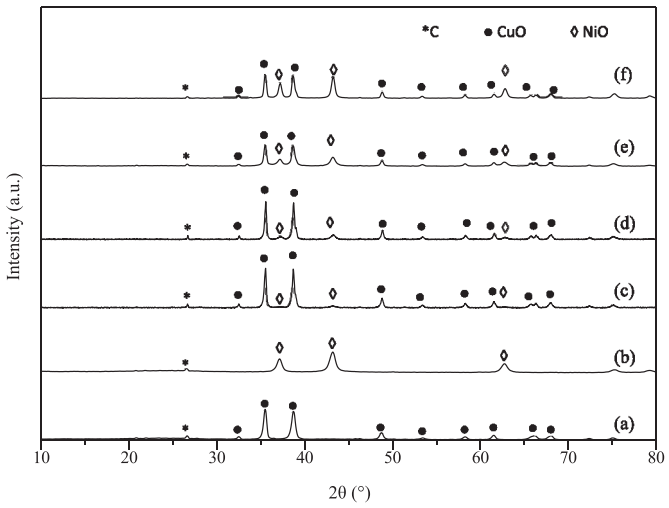

Fig. 1. Powder XRD pattern of (a) Cu/AC (b) Ni/AC (c) $CuNi_{0.1}$/AC(d) $CuNi_{0.2}$/AC (e) $CuNi_{0.5}$/AC and (f) $CuNi_1$/AC catalyst.

XRD patterns of single metal Cu/AC and single metal Ni/AC catalyst were also studied for comparison with the $CuNi_x$/AC catalysts. For Cu/AC catalyst, three major peaks could be observed at 2θ = 35.5°, 38.7° and 48.7° which were attributed to $(\bar{1}11)$, (111) and $(\bar{2}02)$ planes, respectively for CuO hexagonal phase of PDF no. 00-045-0937. As for Ni/AC catalyst, three distinct diffraction peaks at 2θ = 37.2°, 43.2° and 62.8° which corresponds to (111), (200) and (220) planes of NiO cubic phase with PDF no. 01-073-1523. All of the $CuNi_x$/AC catalysts had both peaks that correspond to hexagonal CuO and cubic NiO. Peaks of the corresponding phases are indicated by different symbols in Fig. 1.

With increasing Ni content, the peaks shifted to higher angle for both peaks of CuO and NiO phases. This shows that there is an existence of both phases in the crystal lattice. There were also no changes in crystal phase of CuO with the addition of Ni into Cu/AC catalyst. However, the addition of Ni did not lead to distortion of the CuO phase. The peaks correspond to NiO was very weak when Ni was added in small amount. As the amount of Ni increased, the peak intensity which corresponds to CuO decreased while the peak intensity for NiO gradually increased. When the amount of Ni increased to 0.5 mol and 1.0 mol, there were obvious peak broadening occurred. This suggests an influence in peak intensity/width of co-existing phase can be detected. Similar observation was also reported for Cu-Mn catalyst [14].

The crystallite size of the catalysts measured using Scherrer's equation and d-spacing are presented in Table 1. The crystallite size of CuO was found to be larger compared to NiO. This is due to the larger ionic radius of Cu^{2+} (0.72 Å) compared to Ni^{2+} (0.69 Å). As for $CuNi_x$/AC catalysts, the crystallite size range is around 27 nm–37 nm. Although the crystallinity of the catalysts decreased with the increasing amount of Ni, the crystallite size increased gradually. This might be due to crystal strain or defects caused by the addition of Ni. It also suggests there might be a lattice expansion even though Ni^{2+} has a smaller ionic radius. Similar trend was observed for CeO_2 due to the lattice expansion caused by the decreased in electrostatic force in the valence band [22]. However, the d-spacing of the catalysts did not change drastically. The trend in crystallite size suggests that the presence of Ni did not limit the crystal growth.

3.2. Morphology of catalysts

The SEM images of the synthesized catalysts are shown in Fig. 2. For Cu/AC catalyst, it was observed that sphere shaped particles were deposited on the surface of activated carbon. Cu are widely distributed with some particles agglomerated into larger sphere. The particle size was estimated to be in the range of 0.40 μm–1.10 μm. Monometallic Ni/AC catalyst showed undefined shape of small particles on the surface (Fig. 2b). When Ni was added into monometallic Cu/AC catalyst (Fig. 2c–f), the presence of small defined sphere shape could be observed. The morphology of the catalyst remained the same regardless of the amount of Ni added. This suggested that the addition of Ni changes the morphology of the catalyst to be different from both CuO and NiO. Therefore, synergistic interaction between Cu and Ni is eventually established. The particle sizes of $CuNi_x$/AC catalysts range from 0.40 μm to 0.80 μm. The slight decrease of the particles size of Cu/AC catalyst when Ni was added could be attributed to the interactions between two metals, known as stabilizing effect [23] as confirmed by XRD the

Table 1
Crystal properties of the catalysts.

Entry	Catalyst	d-spacing (nm)	Crystallite size (nm)
1	Cu/AC	2.5266	25.1
2	Ni/AC	2.0935	12.5
3	$CuNi_{0.1}$/AC	2.5256	27.3
4	$CuNi_{0.2}$/AC	2.5232	30.9
5	$CuNi_{0.5}$/AC	2.5264	32.3
6	$CuNi_1$/AC	2.5262	37.1

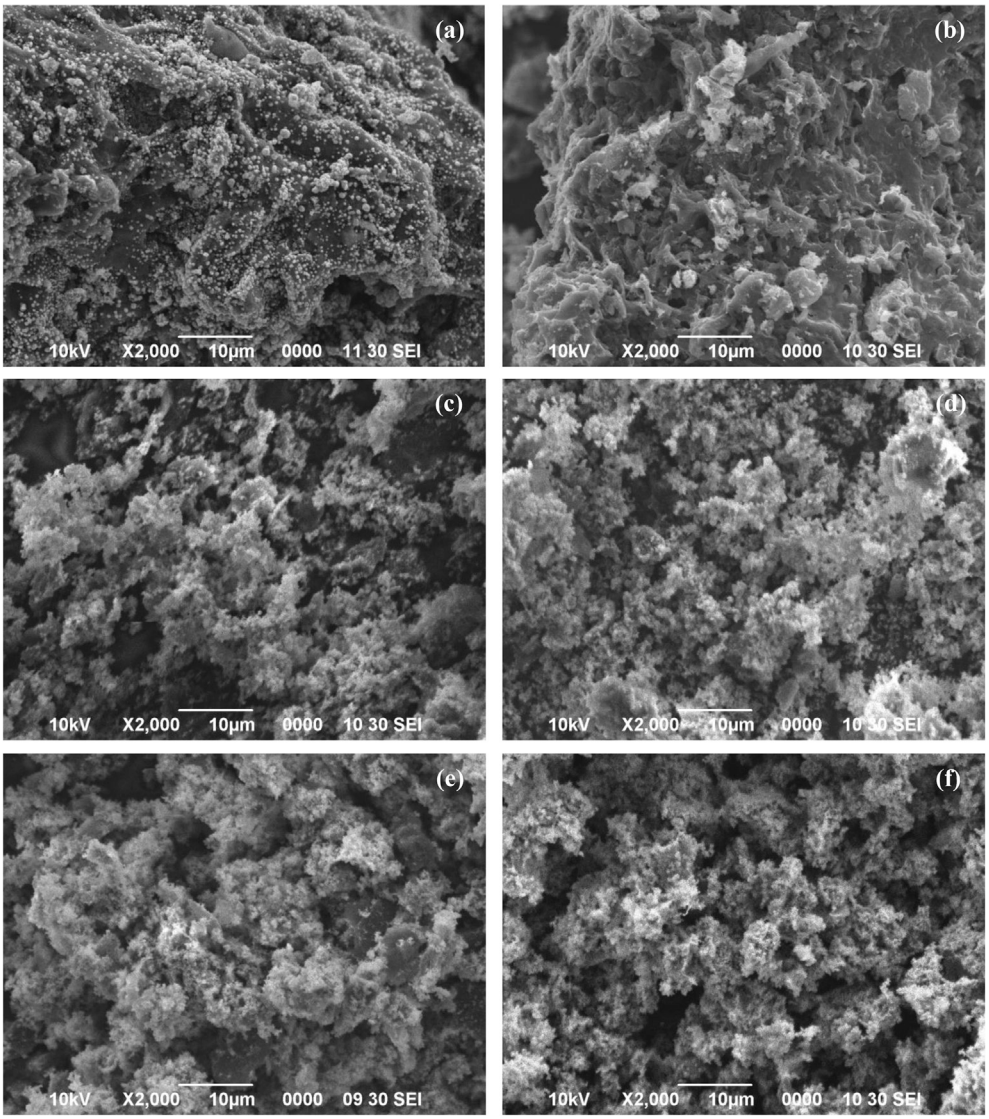

Fig. 2. SEM images of (a) Cu/AC (b) Ni/AC (c) $CuNi_{0.1}$/AC (d) $CuNi_{0.2}$/AC (e) $CuNi_{0.5}$/AC and (f) $CuNi_1$/AC catalyst.

presence of both CuO and NiO phase in the catalysts. The dispersion of the particles was more uniform as compared to monometallic Cu/AC catalyst. Most of the particles of $CuNi_x$/AC catalysts agglomerated into larger particles. However, the surface of AC was not observed due to the presence of Cu and Ni particles on the surface. This shows that both Cu and Ni have large contact area with AC support.

3.3. Catalytic activity of catalysts

The catalytic conversion of Cu/AC, Ni/AC and $CuNi_x$/AC (x = 0.1, 0.2, 0.5, 1) nanoparticles for the oxidation of benzyl alcohol to benzaldehyde were tested for 2 h using H_2O_2 as oxidant and the results are summarized in Table 2. It has been observed in control experiment that the oxidation of benzyl alcohol does not proceed in the absence of catalyst and the conversion of benzyl alcohol on pure AC is very low. However, in the presence of metal oxides on the surface of AC, AC offers site for oxygen activation and regeneration [24], whereas the metal oxides act as site for alcohol dehydrogenation [25]. Thus, when tested, the monometallic Cu/AC and Ni/AC catalyst was active for the oxidation of benzyl alcohol. This showed that the metal catalyst act as effective active sites for the oxidation of benzyl alcohol. However, the conversion rate was low under identical conditions as the bimetallic $CuNi_x$/AC catalysts. When a small amount of Ni was added into Cu/AC catalyst, the conversion of benzyl alcohol to benzaldehyde increased. The bimetallic catalyst shows enhanced activity for this reaction compared to monometallic Cu and Ni catalyst. The enhanced activity can be ascribed to the cooperative effect due to the existence of both CuO and NiO species on AC as identified by XRD. They provide positive effects and showed better performance on the conversion of benzyl alcohol to benzaldehyde. It was reported that CuO oxides interfaces in a bimetallic structure were supposed to be the active sites for the activation of oxygen molecules which enhanced aerobic oxidation reactions [26,27]. The catalytic activity is also dependent on the amount of Ni composition. The benzyl alcohol

Table 2
Catalytic performance of the catalysts for the oxidation of benzyl alcohol to benzaldehyde.

Entry	Catalyst	Conversion (%)
1	Cu/AC	13.8
2	Ni/AC	33.6
3	$CuNi_{0.1}$/AC	35.1
4	$CuNi_{0.2}$/AC	36.5
5	$CuNi_{0.5}$/AC	37.1
6	$CuNi_1$/AC	46.8

Reaction conditions: 0.1 g catalyst, 2.6 mL benzyl alcohol, 3.3 mL H_2O_2, 20 mL toluene as solvent, T = 80 °C, t = 2 h.

conversion increased with increasing Ni content under the same Cu loading. The highest activity was shown by $CuNi_1$/AC catalyst. Notably, bimetallic $CuNi_1$/AC catalyst presented their optimal proportion on the AC support. This demonstrated that the presence of NiO in high amount will increase the number of active sites. Using the deposition-precipitation techniques for synthesis had been shown to exhibit higher dispersion of metal particles [28] which also promotes stability [29]. Furthermore, based on SEM images, the $CuNi_1$/AC catalyst exhibited better dispersion compared to their monometallic counterpart. All these contributed to the best catalytic activity of $CuNi_1$/AC catalyst. Although from XRD analysis was found that $CuNi_1$/AC catalyst showed the least crystallinity, in this case the number of active sites was the major factor affecting the catalytic activity.

4. Conclusions

In summary, $CuNi_x$/AC catalysts was successfully synthesized using deposition-precipitation method. This method enables the catalytic properties to be tuned via controlling the ratio of Cu and Ni. $CuNi_1$/AC catalyst showed superior catalytic performance for benzyl alcohol oxidation to benzaldehyde. The resulting $CuNi_x$/AC bimetallic catalysts are composed of uniformly sphere particles that had different morphology compared to their monometallic Cu/AC and Ni/AC catalyst counterpart. The presence of both Cu and Ni species enhanced the catalytic activity by increasing the number of active sites that participated in the catalytic conversion of benzyl alcohol.

Conflict of interest

The authors declare no conflict of interest.

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